Another look at the water solubility in biodiesels: Further experimental measurements and prediction with the CPA EoS

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ABSTRACT

In a previous work we addressed the importance of knowing and describing the water solubility in biodiesels, for producing high quality biodiesel using the most suitable feedstock and operating the processing plants at the optimal conditions. The lack of information on the water solubility in methyl linoleate limited the quality of the results then reported. To overcome the identified limitations new water solubility measurements were carried out for methyl linoleate and four methylic biodiesels synthesized at our laboratory from the main oil feedstock currently used for biodiesel production (soybean, palm, rapeseed and sunflower oils).

The new experimental data presented here for the water solubility in methyl linoleate allowed to obtain the information about the binary system water/methyl linoleate (specifically the binary interaction parameter, k_{ij}) to be used in the modeling of multicomponent systems (biodiesels) with the CPA EoS. With this new interaction parameter the new experimental water solubilities reported in this work for four biodiesels were predicted with the CPA EoS with global average deviations inferior to 7%.

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1. Introduction

The large number of recent research works addressing the production, characterization and use of biodiesel clearly demonstrate the increasing worldwide importance of this biofuel. Offering the various advantages known to characterize biofuels, sustainability, reduction of greenhouse gases emissions, regional development and secure supply [1], biodiesel is actually the most promising alternative for petroleum based fuels for compressed ignition (diesel) engines. Due to its similarity in chemical structure and energy content with conventional diesel, it can be used in existing engines as pure or blended with regular diesel [2]. In fact, biodiesel, a blend of fatty acid alkyl esters, along with bioethanol, already represents 1.6% of the transport fuel used worldwide [3].

Although most research activities have been addressing different methods to produce biodiesel, involving new feedstock (such as cooking waste oil and microalgae oils [4]), novel catalysts (heterogeneous catalyst and enzymes) [4] and process conditions (supercritical [4]), the actual industrial way to produce biodiesel consists on the transesterification reaction of a vegetable oil with an alcohol (usually methanol [5] or ethanol in countries where this alcohol is easily produced and available [6]) with a basic catalyst, using mild operation conditions. The produced fatty acid

esters cannot be labeled as biodiesel until they meet the EN 14214 [7] quality specifications in Europe, and the ASTM D6751 in the USA. As a consequence, after the transesterification reaction, the fatty acid methyl esters undergo several purification processes in order not to overcome the minimum contents in free glycerol, soap, metals, alcohol, free fatty acids, catalyst, water and glyceride established by the European and American standards. A high presence of these compounds in the biodiesel strongly affects the fuel properties and performance and consequently the engine life.

One of these purification steps is the fatty acid esters washing with hot water. This is the most common method of purification as it is efficient in removing methanol, glycerol, sodium compounds, free fatty acid esters and soaps [8].

However, one of the requirements of the European and American quality standards is the biodiesel water content, since water affects the calorific value of the biodiesel, can cause the esters to react to produce soaps and can cause blocking and wearing of the engine injection system. Water in biodiesel also diminishes the shelf life of the fuel, since it decreases the biodiesel oxidation stability and promotes biological growth [9,10]. Consequently, after being washed with water, the fatty acid esters are dried in order to produce biodiesel with a water content not overcoming the maximum value of 0.05% (w/w) imposed in Europe by the EN 14214.

In the last few years, our research group has been addressing the measurement of phase equilibria and the development of

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Nomenclature

a_0, c_1	parameters for calculating a
b	co-volume
C_n	carbon number
k_{ij}	binary interaction parameters
P	vapor pressure
T	temperature
T_c	critical temperature
x	mole fraction

Greek symbols

β	association volume
ε	association energy

ρ	mole density

List of abbreviations

AAD	average absolute deviation
calc	calculated
CPA	cubic-plus-association
EoS	equation of state
exp	experimental
SRK	Soave–Redlich–Kwong

thermodynamic models for the description of biodiesel production and purification processes [11–17]. Being able to predict the different phase equilibria of the binary and multicomponent systems found during the biodiesel production and purification, in a wide range of thermodynamic conditions, is essential for a correct design and optimization of these industrial processes, through the correct selection of suitable solvents, the most advantageous unit operations and separation sequence and their optimal size and operating conditions.

Two of these studies were focused on the measurement and prediction of the water solubility in pure fatty acid alkyl esters and biodiesels [15,17]. Knowing the water solubility in biodiesels is essential for the biodiesel production and purification processes, allowing tuning the more favorable raw materials and correctly designing and optimizing the biodiesel washing and drying units in order to produce high quality biodiesel in agreement with the European and American quality specifications.

While assessing the poor performance of commonly used thermodynamic models, namely cubic equations of state and activity coefficient models, to describe the water solubility in fatty acid esters and their mixtures [15], the authors also developed and applied a more theoretical sound model, the Cubic-Plus-Association equation of state (CPA EoS), that explicitly describes the specific interactions between like molecules (in this case water) and unlike molecules (cross-association, in this case between esters and water). In an accurate, predictive and simple way, this model proved to be the most appropriate to describe the water solubility in biodiesels [15,17].

Following these studies, in this work, new experimental water solubility measurements were carried out for methyl linoleate and four biodiesels synthesized at our laboratory from edible oils commonly used for producing biodiesel [4]: rapeseed, soybean, palm and sunflower, and the CPA EoS was applied to predict these new experimental data.

As the CPA EoS prediction of the water solubility in biodiesels is performed using interaction parameters obtained from binary phase equilibria data, it was possible, using the new data for methyl linoleate, to evaluate the contribution of this binary system to the improvement of the model prediction capability for the water solubility in biodiesels, by reassessing the results presented before for the water solubility in six commercial biodiesels [17].

2. Experimental section

2.1. Materials

The water solubility was measured in the biodiesels synthesized by the transesterification reaction with methanol of the vegetable oils: soybean, rapeseed, palm and sunflower. The molar ratio of oil/methanol used was 1:5 using 0.5% sodium hydroxide by weight of oil as a catalyst. The reaction was performed at 55 °C during 24 h under methanol reflux. The reaction time chosen was adopted for convenience and to guarantee a complete reaction conversion. Raw glycerol was removed in two steps, the first after 3 h reaction and then after 24 h reaction in a separating funnel. Biodiesel was purified through washing with hot distillated water until a neutral pH was achieved. The biodiesel was then dried until the EN ISO 14214 limit for water was reached [7].

Biodiesels were characterized by GC-FID following the British Standard EN 14103 from EN 14214 [7] to know their methyl esters composition. Capillary gas chromatography was used to determine the methyl ester composition of the biodiesel samples. A Varian CP-3800 with a flame ionization detector in a split injection system with a Select™ Biodiesel for FAME Column, (30 m × 0.32 mm × 0.25 μm), was used to differentiate all methyl esters in analysis inclusively the poli-unsaturated ones. The column temperature was set at 120 °C and then programmed to increase up to 250 °C, at 4 °C/min. Detector and injector were set at 250 °C. The carrier gas was helium with a flow rate of 2 mL/min.

The water solubility was also measured in methyl linoleate (Aldrich, 99%).

2.2. Experimental procedure

The water solubility measurements were carried out at temperatures from 288.15 to 318.15 K and at atmospheric pressure. The methodology used in this work, has already been successfully used for measuring the water solubility in fatty acid esters, biodiesels [17] and fatty acids [12]. The ester and the water phases were initially agitated vigorously and allowed to reach the saturation equilibrium by the separation of both phases in 20 mL glass vials for at least 48 h. This period proved to be the minimum time required to guarantee a complete separation of the two phases and that no further variations in mole fraction solubilities occurred.

The temperature was maintained by keeping the glass vials containing the phases in equilibrium inside an aluminum block specially designed for this purpose, which is placed in an isolated air bath capable of maintaining the temperature within (±0.01 K).

The temperature control was achieved with a PID temperature controller driven by a calibrated Pt100 (class 1/10) temperature sensor inserted in the aluminum block. In order to reach temperatures below room temperature, a Julabo circulator, model F25-HD, was coupled to the overall oven system allowing the passage of a thermostatized fluid flux around the aluminum block. The solubility of water in the ester rich phase was determined using a Metrohm 831 Karl Fischer (KF) coulometer.

The esters rich phase was sampled at each temperature from the equilibrium vials using glass syringes maintained dry and at the same temperature of the measurements. Samples of 0.1–0.2 g were taken and injected directly into the KF coulometric titrator.

The water solubility results at each individual temperature are an average of at least five independent measurements.

3. Model

The Cubic-Plus-Association equation of state (CPA EoS) has been extensively described in the literature and no further details will be explained in this work. For further information please see related works [18–20].

4. Results and discussion

Table 1 reports the methyl ester composition of the four synthesized biodiesels. The methyl esters are presented as CX or as CX:Y where X is the acid chain carbon number and Y is the number of double bonds in the fatty acid chain.

The water solubility results in soybean, rapeseed, palm and sunflower biodiesels and in methyl linoleate, in the temperature range 288.15–318.15 K are listed in Table 2, as well as their respective standard deviations.

The values presented for the water solubility in the biodiesels and in methyl linoleate are in agreement with the results previously presented [17]. As expected, since the water solubility in fatty acid esters increases with the ester insaturation [17], palm biodiesel presents the lowest water solubility, in agreement with its higher content in the saturated ester methyl palmitate. The other biodiesels present quite similar water solubility values, as expected due to their analogous fatty acid ester composition, with the sunflower biodiesel presenting the highest water solubility.

As explained at the introduction section, we have previously applied the CPA EoS to describe the water solubility in fatty acid esters and to predict it in biodiesels [17]. The information gathered in that work will be applied here, as subsequently shown, to predict the experimental results.

Modeling with the CPA EoS starts with the definition of the CPA pure compounds parameters. Esters are non-self-associating compounds and consequently there are only three pure compound parameters from the physical term to be determined: a_0, c_1 and b. These parameters are usually determined from a simultaneous regression of vapor pressure and liquid density data. In a previous work [17] these parameters were estimated for the methyl esters C16:0, C18:0, C18:1, C18:2, which are the major components of commercial biodiesels. Due to the lack of reliable liquid density

Table 1
Compositions of the biodiesels studied, in mass percentage.

Methyl ester	Soybean	Rapeseed	Palm	Sunflower
C10			0.01	0.03
C12		0.04	0.24	0.02
C14	0.07	0.07	0.57	0.07
C16	10.76	5.22	42.45	6.40
C16:1	0.07	0.20	0.13	0.09
C18	3.94	1.62	4.02	4.22
C18:1	22.96	62.11	41.92	23.90
C18:2	53.53	21.07	9.80	64.16
C18:3	7.02	6.95	0.09	0.12
C20	0.38	0.60	0.36	0.03
C20:1	0.23	1.35	0.15	0.15
C22	0.80	0.35	0.09	0.76
C22:1	0.24	0.19	0.00	0.08
C24		0.22	0.15	

Table 2
Experimental results, in molar fractions, for the water solubility in biodiesels and in methyl linoleate.

T/K	$(x_{H_2O} \pm \sigma^a)$
Rapeseed biodiesel	
303.15	0.0303 ± 0.0030
308.15	0.0330 ± 0.0005
313.15	0.0365 ± 0.0002
318.15	0.040 ± 0.001
Soybean biodiesel	
303.15	0.0284 ± 0.0002
308.15	0.0313 ± 0.0005
313.15	0.0351 ± 0.0005
318.15	0.0402 ± 0.0003
Palm biodiesel	
298.15	0.022 ± 0.003
303.15	0.0246 ± 0.0005
308.15	0.0273 ± 0.0005
313.15	0.030 ± 0.008
318.15	0.0322 ± 0.0007
Sunflower biodiesel	
293.15	0.024 ± 0.002
303.15	0.0317 ± 0.0009
308.15	0.0345 ± 0.0002
313.15	0.0369 ± 0.0002
318.15	0.0397 ± 0.0006
Methyl linoleate	
303.15	0.0277 ± 0.0001
308.15	0.0333 ± 0.0007
313.15	0.037 ± 0.001
318.15	0.0420 ± 0.0007

[a] Standard deviation.

data for the unsaturated esters at the time, preference was given to the vapor pressure description.

Recently, using density data for several fatty acid esters and biodiesels [21,22], measured by us, it was possible to re-estimate the CPA pure compound parameters for all the fatty acid methyl esters found in the biodiesel samples considered in this work, compounds ranging from 15 to 25 carbon atoms and with up to three unsaturated bonds (Table 3), by a simultaneous regression of pure component data. Vapor pressures and liquid densities were described with global average deviations inferior to 2% (Table 3).

Having the CPA pure compound parameters it was then possible to predict the water solubility in the ester multicomponent systems considered here. The k_{ij}s for ester/ester were set to zero and, as already stated above, the solvation phenomena between the non-self-associating ester and the self-associating water was considered as a cross-association within the framework of the CPA EoS, where the cross-association energy (ε_{ij}) was considered to be half the value of the association energy for the self-associating component (in this case water) and the cross-association volume (β_{ij}) was left as an adjustable parameter, fitted to the equilibrium data along with the k_{ij}.

When describing the water solubility in different fatty acid esters [17], a constant value for the cross-association volume, β_{ij}, was established (of 0.201), as well as a linear correlation for calculating the k_{ij}s between esters and water was found with the chain length of the ester, C_n:

$$K_{ij} = 0.0136 \, C_n - 0.3322 \tag{1}$$

This correlation, and the constant value for the cross-association volume, allowed predicting the water solubility in six commercial biodiesels from GALP, with global average deviations inferior to 15% [17]. Only for the k_{ij} between water and methyl oleate it was used the regressed value from phase equilibria data since it did not fit in the linear dependency with the carbon number determined for the saturated methyl esters. In addition, as phase

Table 3
Fatty acid methyl esters critical temperatures computed from the Wilson and Jasperson group contribution method for saturated methyl esters and from the Ambrose method for unsaturated methyl esters, CPA pure compound parameters and modeling results [23].

Methyl ester	Tc (K)	a_0 (J m^3 mol^{-2})	c_1	$b \times 10^4$ (m^3 mol^{-1})	AAD%	
					P	ρ
C12	710.41	6.7139	1.5340	2.3010	0.83	0.60
C14	740.97	8.0272	1.6089	2.6361	0.45	0.52
C16	765.92	7.4198	2.2873	2.9749	1.46	0.62
C16:1	749.63	9.2554	1.7805	2.9564	2.38	1.21
C18	788.63	10.1303	1.9196	3.3111	0.39	0.68
C18:1	772.34	10.5075	1.8212	3.2485	0.81	0.74
C18:2	786.37	8.9943	2.1597	3.1714	1.37	0.66
C18:3	797.26	8.6712	2.1722	3.0949	1.18	1.03
C20	803.28	13.4696	1.6123	3.7121	0.78	0.85
C20:1	786.99	12.5293	1.7143	3.5792	5.98	1.22
C22	817.47	16.2713	1.4963	4.0503	0.34	0.71
C22:1	801.18	15.3112	1.5933	3.9168	4.73	1.86
C24	830.41	19.3150	1.4045	4.3953	0.13	0.65
[a]Global AAD%					1.60	0.87

[a] Global $AAD\% = \frac{1}{N_s} \sum_{i=1}^{N_s} \left| \frac{exp_i - calc_i}{exp_i} \right| \times 100$, where N_s is the number of data points studied.

Table 4
Deviations in the mole fraction water solubility from CPA (the first column represents deviations using the recently assessed pure compounds and binary parameters and the second column previous results from Ref. [17]).

Compound	AAD%	Former results [17] AAD%
Methyl linolenate	3.4	
Rapeseed biodiesel	10.5	
Soybean biodiesel	3.9	
Palm biodiesel	6.3	
Sunflower biodiesel	9.4	
Global AAD %	6.7	
Biodiesel A	11.0	18.6
Biodiesel B	11.9	15.8
Biodiesel C	15.4	18.4
Biodiesel D	11.4	13.3
Biodiesel E	12.5	16.9
Biodiesel F	5.3	9.8
Global AAD%	11.3	15.5

Global $AAD\% = \frac{1}{N_s} \sum_{i=1}^{N_s} \left| \frac{exp_i - calc_i}{exp_i} \right| \times 100$ where N_s is the number of data points studied.

Fig. 1. Water solubility in methyl linoleate: symbols experimental results and solid line CPA EoS results ($k_{ij} = -0.130$).

equilibria data for the water/methyl linoleate system was not available at that time, the k_{ij} value for this sub-binary system was made equal to the one established for the water/methyl oleate system.

In this work, having measured the water solubility in methyl linoleate, the corresponding k_{ij} interaction parameter was determined, using the same constant value for the cross-association volume referred before. A k_{ij} value of −0.13 was obtained, describing the water solubility with global average deviations inferior to 3% (Table 4 and Fig. 1).

The experimental water solubility in the soybean, rapeseed, palm and sunflower biodiesels were then predicted using the recently assessed CPA pure compound parameters for esters and the previously proposed linear correlation to estimate the interaction parameters between the different saturated fatty acid methyl esters constituting the biodiesels and water, with global average deviations inferior to 7% for these four biodiesels (Table 4). For the binary sub-systems containing water and methyl oleate and linoleate the interaction parameter values regressed from phase equilibria data were used (from an earlier work for methyl oleate [17] ($k_{ij} = -0.100$) and from the present study for methyl linoleate ($k_{ij} = -0.130$)), as they did not fit in the linear correlation proposed
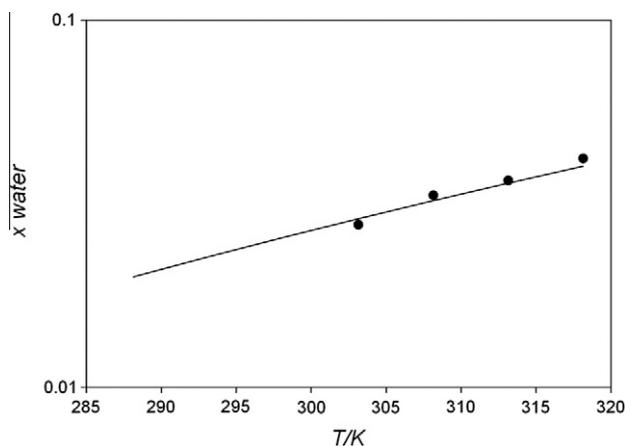
for saturated methyl esters. For methyl linolenate, the unsaturated fatty ester in less percentage in the selected biodiesels, the same k_{ij} value used for methyl linoleate was applied.

Prediction results are depicted in Fig. 2 for the palm and soybean biodiesels.

The strength of the solvation phenomena between water and esters is clearly showed by the relatively high values of the binary interaction parameters needed. In fact, as previously showed [17], the model must explicitly take into account the cross-association between esters and water, since without it, the calculated water solubilities are much lower than the experimental values.

These set of pure and binary parameters were also applied in this work to predict the water solubility in the GALP biodiesels addressed previously (Biodiesel A–F in Table 4). The global average deviations for the water solubility in these six biodiesels previously estimated to be 15% [17] were reduced in this work to 11% (biodiesels A–F in Table 4). It must be pointed out that the improvement on these results is mainly due to the use of a regressed k_{ij} value for the binary sub-system water/methyl linoleate, instead of using the same value obtained for the methyl oleate/water sub-system as previously done [17], and not as much due to the use of new CPA pure compound parameters for esters, since it was verified that the regressed binary interaction parameters obtained are quite independent of the CPA pure
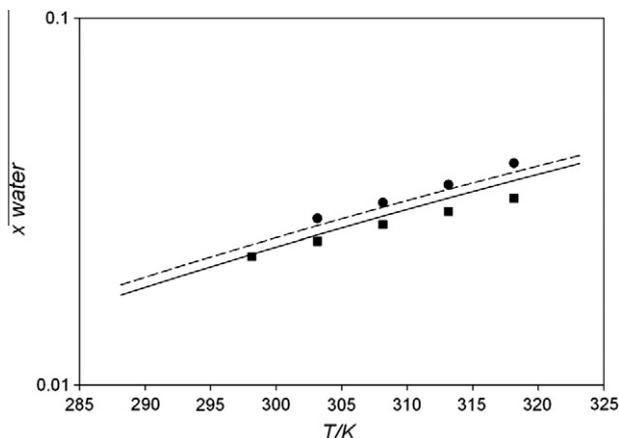
Fig. 2. Water solubility in palm biodiesel (■, experimental results; solid line CPA EoS results), and in soybean biodiesel (●, experimental results; dashed line CPA EoS results).

compound parameters used for esters, leading to the same global average deviations for the water solubility in biodiesels obtained before if no specific k_{ij} value is used for the water/methyl linoleate sub-system.

This demonstrates the importance that the right description of unsaturated ester systems can have on the modeling of the water solubility in biodiesels.

5. Conclusions

Biodiesel is seen as one of the most important alternatives to conventional fuels since its use can solve the range of environmental, economic and political problems related to the use of conventional petroleum based fuels.

The water content in biodiesel have significant effects on the fuel quality and performance and so the ability to predict this property is essential for dimensioning biodiesel production and purification processes and optimizing their operation within product specifications.

Here new experimental measurements were performed for the water solubility in methyl linoleate and four methylic biodiesels synthesized from oils constituting the principal feedstock currently used for biodiesel production.

The water solubility in the soybean, palm, rapeseed and sunflower biodiesels was predicted with the CPA EoS with global average deviations inferior to 7%.

Acknowledgments

The program used to perform the calculations with the CPA EoS is available at: <http://path.web.ua.pt/biodiesel.asp>.

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